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Nonlinear Optical Properties of TeO₂-Based Glasses : RO-TeO₂ (R=Mg, Sr and Ba) Binary Glasses

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The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, of $x\text{RO} \cdot (100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) binary glasses have been measured with a special attention to the effect of addition of second component using the third harmonic generation (THG) method. The $\chi^{(3)}$ value obtained is for example, 9×10^{-13} esu for 10BaO-90TeO₂ glass. It is found that the third-order nonlinear optical susceptibilities $\chi^{(3)}$ of alkaline-earth oxide containing TeO₂ glasses decrease drastically with increasing alkaline-earth oxide content, corresponding to the decrease in the polarizability in unit volume. An excellent linear relationship is found to hold between the $\chi^{(3)}$ and $(n_\omega^2 + 2)^3 \cdot (n_\omega^2 - 1) \cdot E_d/E_0^2$ irrespective of kind of alkaline earth metals.

KEY WORDS: Third-order nonlinear optical susceptibilities/ $\chi^{(3)}$ / Alkaline-earth oxide containing TeO₂ glasses

1. INTRODUCTION

TeO₂-based glasses have attracted much attention as photonic materials.¹⁻³⁾ TeO₂ itself has been found to be a superior photonic material having a large $\chi^{(3)}$ value of 1.4×10^{-12} esu.⁴⁾ The problem of this glass is that only a small piece of glass is produced even by a rapid quenching technique. Therefore, it is absolutely required to add second components in order to obtain a large piece of glass. Fortunately, TeO₂ is known to form a glass with a variety of metal oxides and halides over a relatively wide composition range.^{5,6)}

In this respect, it is of essence to investigate the influence of addition of each second component on the nonlinear optical properties of TeO₂-based glasses in order to develop glass materials applicable to photonic devices. In this paper, we will deal with the effect of alkaline earth oxide as a second component. Especially, the relationship between $\chi^{(3)}$ and optical parameters is discussed on the basis of semiempirical formula.

2. EXPERIMENTALS

The batch compositions of the binary $x\text{RO} \cdot (100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) glasses prepared in this study are shown in Table 1. A 10 g batch of well mixed oxides was melted in a Pt-5% Au crucible at 700–800°C in an ambient atmosphere. The melts were poured into a brass mold and quenched to room temperature. After annealing at 200°C, the glasses were cut into a plate of $10 \times 10 \times 2$ mm³ in size. Both faces were optically polished to eliminate a light scattering

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Nonlinear Optical Properties of TeO₂-Based Glasses

Table 1. Nonlinear optical properties of $x\text{RO} \cdot (100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) binary glasses.

Glass $x/\text{mol}\%$	Density $/\text{gcm}^{-3}$	n_ω	$n_{3\omega}$	E_0 $/\text{eV}$	E_d $/\text{eV}$	R_m/V_m	l_c $/\mu\text{m}$	$T_{3\omega}$ $\%$	T_ω $\%$	$I_{3\omega, \text{Sample}}$ $/\text{a.u.}$	$\chi_{-13}^{(3)\text{exp}}/\text{esu}$
$x\text{MgO} \cdot (100-x)\text{TeO}_2$ glasses											
$x=10$	5.380	2.050	2.106	7.12	22.6	0.516	5.66	79.9	85.7	5.8	5.46
$x=15$	5.315	2.010	2.063	7.31	22.0	0.503	5.98	82.0	87.5	5.1	4.45
$x=20$	5.202	2.003	2.053	7.34	21.9	0.501	6.33	79.2	85.3	4.0	3.90
$x\text{SrO} \cdot (100-x)\text{TeO}_2$ glasses											
$x=10$	5.528	2.054	2.118	6.75	21.5	0.518	4.95	74.1	75.9	6.0	7.95
$x=15$	5.434	2.015	2.073	6.92	20.9	0.505	5.46	74.3	77.4	4.9	6.11
$x\text{BaO} \cdot (100-x)\text{TeO}_2$ glasses											
$x=10$	5.593	2.055	2.119	6.71	21.4	0.518	4.95	78.9	81.2	10.0	9.0
$x=15$	5.556	2.042	2.106	6.76	21.2	0.556	4.95	79.2	81.0	6.1	6.9
$x=20$	5.526	2.006	2.063	6.92	20.8	0.526	5.56	79.3	81.6	6.0	5.8

at the surface. The thickness of glasses for THG and transmittance measurement was 1.0 ± 0.05 mm.

The refractive index of each glass was measured over a wide wavelength range from 486 to 1,000 nm by Mizojiri Optical Works model DVA-36VW ellipsometer.

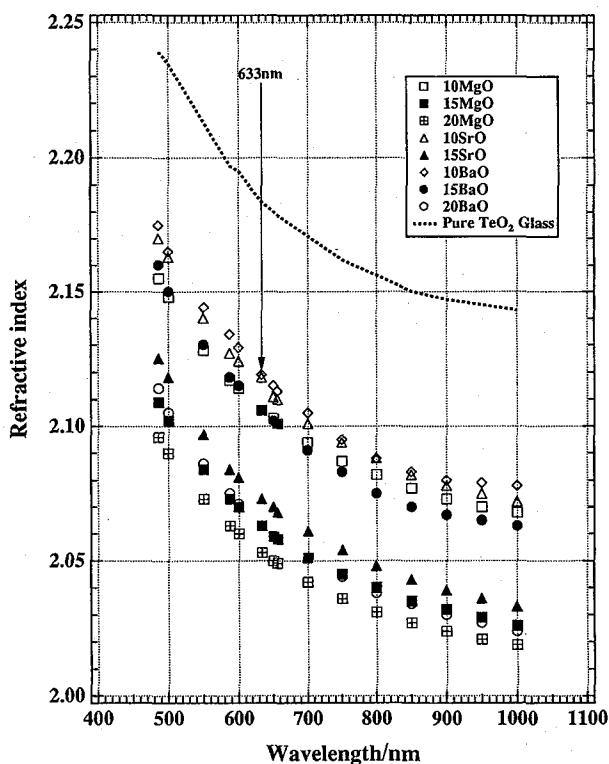


Fig. 1. Variation of refractive index with wavelength in $x\text{RO} \cdot (100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) binary glasses.

The transmittance of glasses was determined in the wavelength range from 200 to 2,000 nm by a Hitach model U-3500 spectrophotometer.

The density was measured by the Archimedes method using kerosene as an immersion liquid at 22°C.

The $\chi^{(3)}$ values were determined by the third harmonic generation (THG) method, using a nonlinear optical measurement apparatus assembled by Tokyo Instruments, Inc., Tokyo, Japan. Further details of the THG measurements are described in our previous papers.^{2,4,7)}

3. RESULTS

As shown in Fig. 1, the refractive indices n of $x\text{RO} \cdot (100-x)\text{TeO}_2$ ($R=\text{Mg}$, Sr and Ba) binary glasses are plotted as a function of wavelength ranging from 486 to 1,000 nm. In all

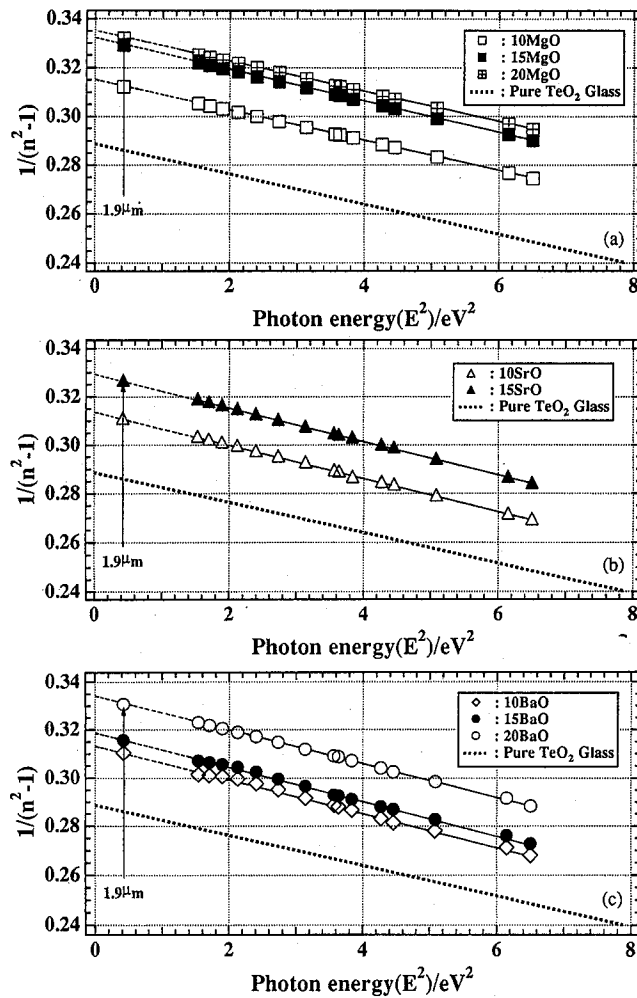


Fig. 2. Dependence of refractive index on photon energy in $x\text{RO} \cdot (100-x)\text{TeO}_2$ glasses: (a) $R=\text{Mg}$ ($x=10, 15$ and 20), (b) $R=\text{Sr}$ ($x=10$ and 15) and (c) $R=\text{Ba}$ ($x=10, 15$ and 20).

cases they monotonously decrease with increasing wavelength. Figure 2(a)–(c) show the plots of $1/(n^2-1)$ vs. E^2 according to the following equation proposed by Wemple.⁸⁾

$$\frac{1}{n^2-1} = \frac{E_0}{E_d} - \frac{E^2}{E_d E_0} \quad (1)$$

where E_d is the dispersion energy and E_0 the excitation energy. Fairly well linear relations between them are observed. The parameters E_0 and E_d obtained from these linear relations are tabulated in Table 1.

Figure 3 shows the refractive indices at 1,900 nm (n_ω) and 633 nm ($n_{3\omega}$) as a function of RO content. For comparison, the values of n_ω and $n_{3\omega}$ of pure TeO₂ glass are also plotted which are cited from ref. 4. In all cases, the addition of RO to TeO₂ reduces the refractive index of TeO₂ glass in the order, BaO > SrO > MgO.

Figure 4(a) and (b) show the composition dependences of the molar volume V_m obtained from density measurements and the molar refraction R_m defined as,⁹⁾

$$R_m = V_m[(n_\omega^2 - 1)/(n_\omega^2 + 2)] \quad (2)$$

where n_ω is the refractive index. The addition of BaO slightly increases the V_m of TeO₂ glass. The addition of SrO does not seem to change the V_m of TeO₂ glass. The R_m 's of TeO₂ decrease with RO content in the order BaO > SrO > MgO. The R_m/V_m , which means the polarizability

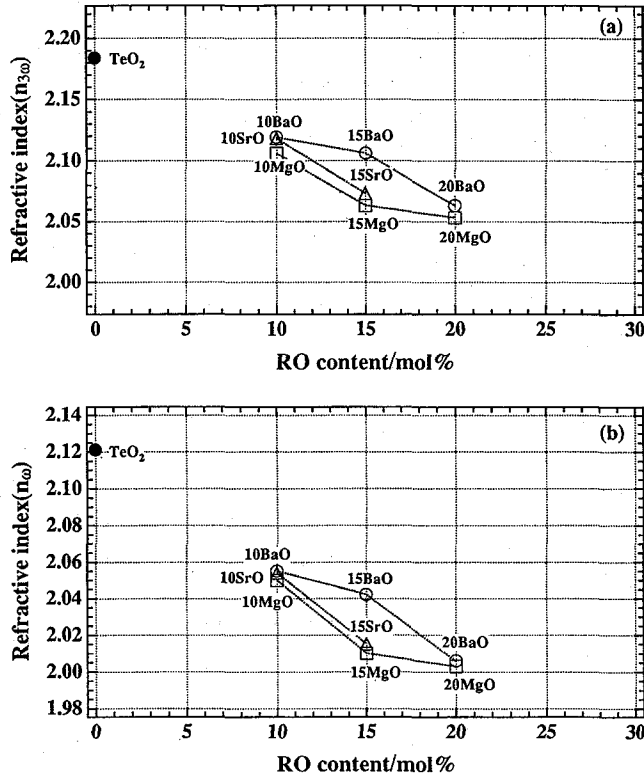


Fig. 3. Variation of linear refractive index at 633 nm (n_ω) and 1,900 nm ($n_{3\omega}$) with RO (R=Mg, Sr and Ba) content in RO-TeO₂ binary glasses.

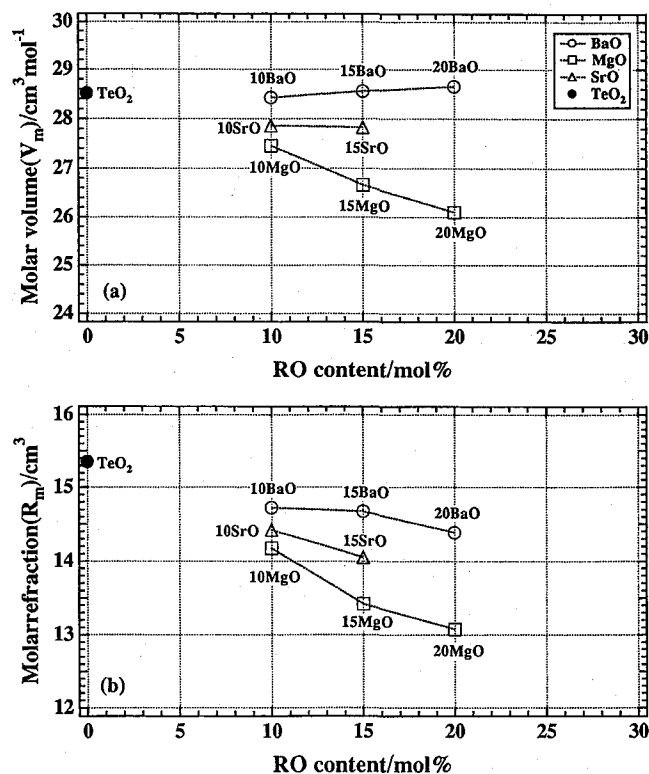


Fig. 4. Composition dependences of (a) Molar volume (V_m) and (b) Molar refraction (R_m) in $x\text{RO} \cdot (100-x)\text{TeO}_2$ ($R=\text{Mg}, \text{Sr}$ and Ba) binary glasses.

per unit volume, is plotted against RO contents in Fig. 5. In each of glass systems, the values decrease with RO contents.

The third-order nonlinear optical susceptibilities, $\chi^{(3)}$, determined from the third harmonic generation intensity $I_{3\omega}$ are shown in Fig. 6. In all cases, the $\chi^{(3)}$ values decrease with RO content in the order $\text{BaO} > \text{SrO} > \text{MgO}$.

4. DISCUSSION

The addition of alkaline earth oxides, MgO, SrO and BaO, has been found to decrease both the refractive index and $\chi^{(3)}$ of TeO_2 glass. It is therefore concluded that although these oxide components have a positive effect in that they extend the glass forming region of TeO_2 -based glasses to a considerable extent, they do not improve the linear and nonlinear optical properties of TeO_2 -based glasses at all.

Fig. 7 shows a relation between the $\chi^{(3)}$ and n_ω . It is interesting to note that the $\chi^{(3)}$ values are much lower in $\text{MgO}-\text{TeO}_2$ glasses than in SrO and $\text{BaO}-\text{TeO}_2$ glasses even though their n values are the same. In the latter two glass systems, they have almost the same $\chi^{(3)}$ values when the n values are the same. Figure 8 shows a relation between the $\chi^{(3)}$ and $(R_m/V_m)^4$. Although the $\chi^{(3)}$ increase with increasing $(R_m/V_m)^4$, a unique straight line can not be fitted to the data,

Nonlinear Optical Properties of TeO₂-Based Glasses

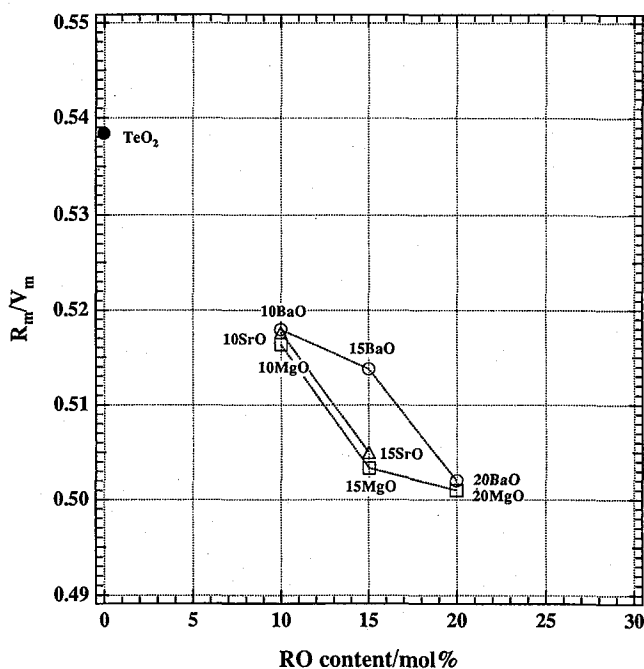


Fig. 5. Polarizability per unit volume (R_m/V_m) of $x\text{RO} \cdot (100-x)\text{TeO}_2$ ($R=\text{Mg, Sr and Ba}$) binary glasses as a function of RO content

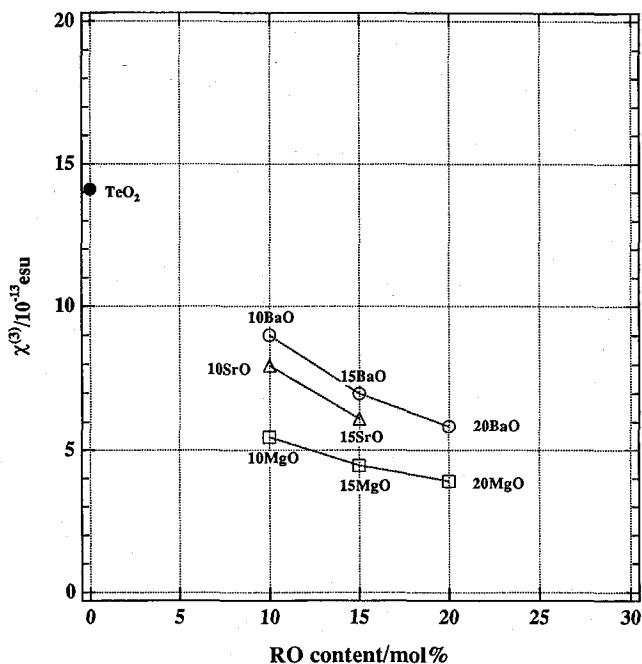


Fig. 6. The third-order nonlinear optical susceptibility $\chi^{(3)}$ of $x\text{RO} \cdot (100-x)\text{TeO}_2$ ($R=\text{Mg, Sr and Ba}$) binary glasses as a function of RO content.

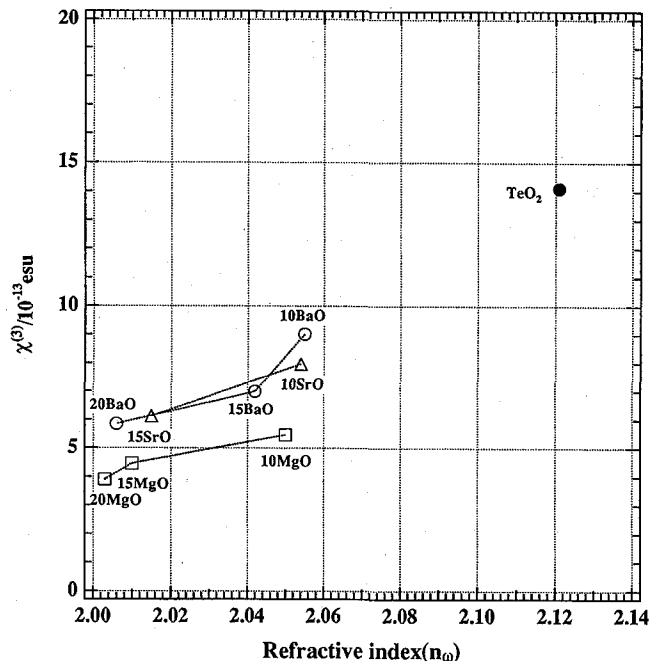


Fig. 7. Relationship between the $\chi^{(3)}$ and linear refractive index (n_ω).

indicating that the generalized Miller's rule^{10,11)} does not strictly hold in these glasses. It should be also noted that the MgO-TeO₂ glasses exhibit a different behavior from other glasses just like in Fig. 7.

As stated above, $\chi^{(3)}$ of MgO-TeO₂ glasses is much smaller than that of SrO-TeO₂ and BaO-TeO₂ glasses. This may reflect that MgO-TeO₂ glasses have unit structures different from SrO or BaO-TeO₂ glasses. In fact, Sekiya *et al.*¹²⁾ reported based on the Raman spectroscopy that the structural units contained in SrO and BaO-TeO₂ glasses are very similar to each other, while those in MgO-TeO₂ glasses are quite different from the case for SrO and BaO-TeO₂ glasses. In SrO- and BaO-TeO₂ glasses, isolated structural units, such as Te₂O₅²⁻ and TeO₃²⁻ ions, coexist with a continuous network composed of tellurium-oxygen polyhedra. In MgO-TeO₂ glasses, the coordination state of tellurium atom changes in analogy with the case of BaO-TeO₂ glasses, but a new structural unit, (Te₃O₈⁴⁻)_n, found in Pb₂Te₃O₈, Nb₂Te₃O₁₁, Mg₂Te₃O₈ and Zn₂Te₃O₈, is formed in high MgO content glasses.

Figure 9 shows a relation between the $\chi^{(3)}$ and the term $(n_\omega^2 + 2)^3 \cdot (n_\omega^2 - 1) \cdot E_d / E_0^2$, which was originally derived by Lines¹³⁻¹⁴⁾ based on the bond orbital theory¹⁵⁻¹⁶⁾ and modified by the present authors^{2,4)}. A good linear relationship between two is observed. A discrepancy, as in Fig. 7 and 8, is not observed in this case. These means that the relation in Fig. 9 is more universal than the relations between the $\chi^{(3)}$ and n or $(R_m/V_m)^4$, and useful to predict the $\chi^{(3)}$ value from these measurable parameters, n , E_d and E_0 .

5. CONCLUSION

Linear and nonlinear optical properties of $x\text{RO} \cdot (100-x)\text{TeO}_2$ (R=Mg, Sr and Ba) glasses

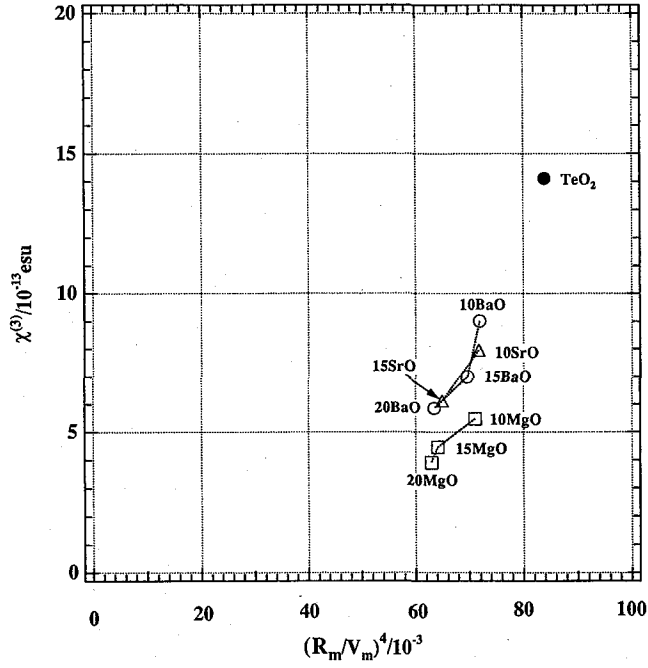


Fig. 8. Relationship between the $\chi^{(3)}$ and $(R_m/V_m)^4$.

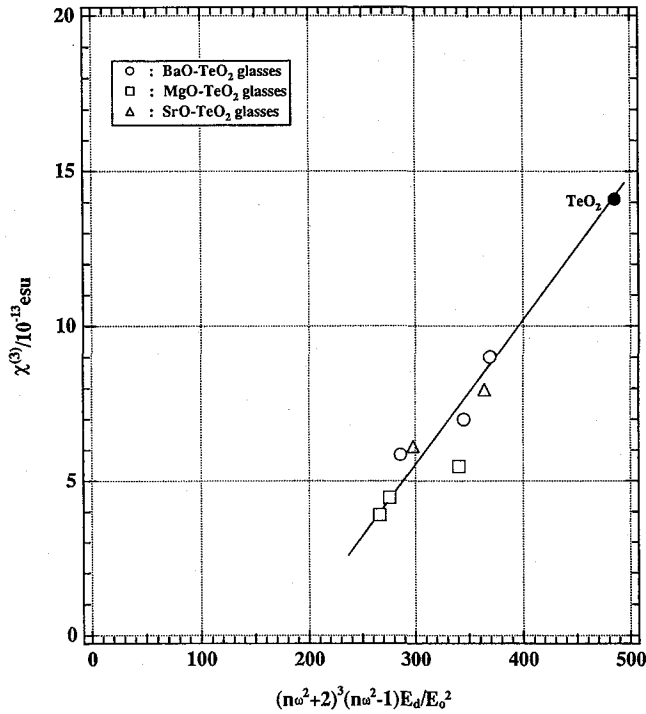


Fig. 9. Relationship between the $\chi^{(3)}$ and the term $(n_{\omega^2}+2)^3 \cdot (n_{\omega^2}-1) \cdot E_d/E_0^2$.

have been measured. The results obtained are summarized as follows.

(1) Alkaline earth oxides, such as MgO, SrO and BaO deteriorate both the linear and nonlinear optical properties of TeO₂ glasses, although they extend the glass forming region.

(2) The structure of MgO-TeO₂ glasses may possibly be different from that of SrO- and BaO-TeO₂ glasses which have a basically similar structure to each other and both contain isolated structural units of Te₂O₅²⁻ and TeO₃²⁻. The difference in glass network structure is reflected on the linear relationship between the $\chi^{(3)}$ and linear refractive index or $(R_m/V_m)^4$.

(3) The modified Lines relationship, $\chi^{(3)} \propto (n_\omega^2 + 2)^3 \cdot (n_\omega^2 - 1) \cdot E_d/E_0^2$, was found to hold for the alkaline earth tellurite glasses irrespective of the kind of the alkaline earth metal.

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